# POLAROGRAPHIC STUDY OF THE CONDUCTION OF THE POLAR EFFECT OF A SUBSTITUENT THROUGH THE FURAN RING AND SIDE BRIDGE GROUPINGS

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The coefficients of conduction of the polar effect of a substituent through the furan ring and side bridge groupings were calculated by comparison of the polarographic half-wave potentials for the electroreduction of the nitro group in series of 5-substituted derivatives of 2-nitrofuran and p-substituted nitrobenzene derivatives by means of the $\rho-\rho$ method. The polarographic method can be successfully used for this purpose in media in which the electrochemical process is not limited by the kinetics of the side process of surface protonation of the nitro group. It follows from the polarographic data and hyperfine structure of the ESR spectra of the anion radicals that the furan ring conducts the polar effect of substituents better (by a factor of 1.1-1.2) than the benzene ring. Depending on the electronic structure of the bridge groups, the introduction of bridge groups between the furan ring and the substituent decreases the conduction of the effect of substituents.

One of the proofs of the heteroaromatic nature of the furan ring is the high coefficient of conduction of the polar effect of substituent X through the furan ring, a value that is close to that of the corresponding value for the benzene ring [1]. On the basis of an analysis of the PMR spectra, for example, it has been shown that the conduction of the total polar effect from the 2 position to the 5 position in the furan ring exceeds the transmission of the total polar effect through the benzene ring in the p position by a factor of 1.2 [2].

The conduction of the polar effect can be estimated by the so-called $\rho-\rho$ method by comparison of the Hammett $\rho$ constants, which reflect the sensitivity of any physicochemical parameter (dissociation constants, reaction rate constants, polarographic half-wave potentials, vibrational frequencies, etc.) to the polar effect of substituent X in two related reaction series, one series of which is taken as the standard [3]. In the present paper a comparative study of the conduction of the polar effect of benzene and furan rings and several side bridge groups was made by means of a modified $\rho-\rho$ method on the basis of polarographic data, namely, from the half-wave potentials ($E_{1/2}$) for the electrochemical reduction of the nitro group in the reaction series of 5-substituted 2-nitrofuran and nitrobenzene derivatives.

It has previously been demonstrated that the $E_{1/2}$ values in series of 5-substituted nitrofurans and p-substituted nitrobenzenes correlate linearly with the Hammett $\sigma$ constants of substituent X [4-8]:

$$\Delta E_{1/2} = E_{1/2}{}^{X} - E_{1/2}{}^{H} = \rho_{\pi}\sigma_{X}\ , \qquad (1)$$

where $\rho_{\pi}$ is a constant (measured in volts) that characterizes the sensitivity of a given electrode reaction to the polar effect of substituent X.

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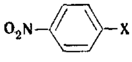
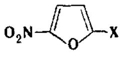
TABLE 1. Ratios of the $\rho_\pi$ Constants of Reaction Series I and II in Aqueous-Alcohol Media

| $C_2H_5OH$ concn. in aqueous-alcohol mixture, % | $\rho_{\pi,\text{fur}}/\rho_{\pi,\text{benz}}$ at pH | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2,0 | 3,0 | 4,0 | 5,0 | 6,0 | 7,0 | 8,0 | 9,0 | 12,0 |
| 0 | 0,7 | 1,0 | 1,0 | 1,1 | 1,3 | 1,1 | 1,2 | 1,2 | 1,1 |
| 10 | 0,9 | 1,0 | 1,2 | 1,2 | 1,1 | 0,9 | 1,2 | 1,1 | 1,1 |
| 20 | 0,7 | 1,0 | 1,2 | 1,0 | 0,6 | 0,6 | 0,6 | 0,6 | 1,1 |
| 40 | 1,5 | 1,6 | 0,8 | 0,8 | 0,6 | 0,7 | 0,6 | 0,6 | 1,0 |
| DMF | 1,1 | | | | | | | | |

A linear correlation between $E_{1/2}$ and the $\sigma_X$ constants in the series named above is observed for different pH values and solution compositions, but the numerical values of the $\rho_\pi$ constants depend markedly on the experimental conditions. We therefore made our comparisons from the magnitudes of the $\rho_\pi$ constants referred to identical experimental conditions.

The following reaction series were studied:


I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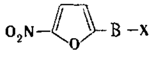
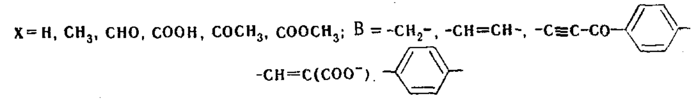

III

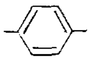
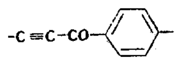

X = H, $CH_3$, CHO, COOH, $COCH_3$, $COOCH_3$; B = $-CH_2-$, $-CH{=}CH-$, $-C{\equiv}C-CO-$

$-CH{=}C(COO^-)$

The relative values of the $\rho_\pi$ constants in series I and II, which were obtained for different experimental conditions, are presented in Table 1. The conduction (z) of the electronic effects through the furan system was characterized by the ratio of the numerical values of the $\rho_\pi$ constants for series I and II, during which series I was taken as the standard. It is seen from the data in Table 1 that z has a constant value of 1.1-1.2 in aqueous media at pH < 3 and in aqueous-alcohol media containing a low percentage of alcohol (up to 10%). This value is in agreement with the ratio of the conduction of the polar effect of substituent X through the benzene ring (1,4 position) and through the furan ring (2,5 position) that was found by comparison of the chemical shifts in the PMR spectra of the corresponding compounds (z = 1.14) [2] and by comparison of the dissociation constants of substituted benzoic and furancarboxylic acids (z = 1.2) [9]. The same value (z = 1.16) was also obtained in a comparison of the $a_N^{NO_2}$ splitting constants of the ESR spectra of the anion radicals of the nitrobenzene and 5-nitrofuran series (the anion radicals were generated by an electrochemical method in aqueous media directly in the resonator of the ESR spectrometer [10, 11]). The $\rho_{\pi,\text{fur}}/\rho_{\pi,\text{benz}}$ ratio is not constant in aqueous-alcohol media in which the alcohol concentration reaches 40% nor in the medium pH range (4-9), even when the alcohol content is 20%. This is associated with the previously established [6, 7] complex character of the dependence of the $\rho_\pi$ constant on the conditions of the medium and with the sharp change in the mechanism of the electrochemical reduction in the medium pH range. Because of the different adsorbabilities of the depolarizer and solvent molecules on the mercury electrode surface and the differences, under the same conditions, in the surface protonation of the nitro compounds, the character of the curves of the dependence of the $\rho_\pi$ constant on the pH is different for series I and II, and a comparison of the $\rho_\pi$ constants in this pH range therefore does not reflect the effect of the electronic structure of the molecules. Consequently, only polarographic data obtained under the conditions of the absence of a limiting effect of side processes (prior and subsequent surface protonation) can be used for the estimation of the coefficient of conduction ($\rho_{\pi,\text{fur}}/\rho_{\pi,\text{benz}}$). In aqueous-alkaline media and in dimethylformamide (DMF), which satisfy the condition mentioned above, the $\rho_{\pi,\text{fur}}/\rho_{\pi,\text{benz}}$ ratio is 1.1, which is in agreement with the results obtained by other methods.

Proceeding from the above, these two media (aqueous alkali and DMF) were also selected to estimate the transmission of the polar effect through bridge grouping B, situated between the 5-nitrofuran grouping and substituent X. In [5] we presented preliminary data on the conduction of the $-CH_2-$ and $-CH{=}CH-$ groupings obtained from the results of polarographic experiments. It is seen from Table 2 that when groupings such as vinylene, methylene, phenylene, etc. are introduced between the ring and substituent, the effect of substituents X on the electrically active center is reduced substantially; this is expressed in a decrease in the values of the $\rho_\pi$ constants of series III as compared with series II, which is taken as the standard in this case.

TABLE 2. $\rho_\pi$ Constants and Attenuation Factors ($Z_B$) Calculated for Reaction Series II and III

| Reaction series III, -B- | $H_2O$, pH 12 | | | DMF | | |
|---|---|---|---|---|---|---|
| | $\rho_\pi$, V | $r$ | $z_B$ | $\rho_\pi$, V | $r$ | $z_B$ |
| - (Reaction Series II) | 0,25 | 0,99 | 1,00 | 0,50 | 0,97 | 1,00 |
| —$CH_2$— | 0,10 | 0,91 | 0,40 | — | — | — |
| —CH=CH— | 0,16 | 0,96 | 0,60 | 0,25 | 0,98 | 0,50 |
| —CH=C(COO⁻)— | 0,12 | 0,97 | 0,51 | 0,22 | 0,97 | 0,44 |
|  | — | — | — | 0,16 | 0,94 | 0,32 |
|  | — | — | — | 0,08 | 0,92 | 0,16 |

Quantitatively, the conduction of bridge groups B can be characterized by the magnitude of the attenuation factor ($Z_B$):

$$z_B = \frac{\rho_\pi^B}{\rho_\pi^0}, \quad (2)$$

where $\rho_\pi^B$ is the value of the constant for the series of derivatives that have a bridge grouping (series III in this case), and $\rho_\pi^0$ is the value of the constant for the series of derivatives without a bridge grouping (series II in this case).

The $Z_B$ values that we calculated for several bridge groups are in agreement with the z values calculated both on the basis of polarographic measurements in other series [12] and those obtained on the basis of analysis of other parameters [13]. It is seen that the decrease in the effect of the substituent on the reaction center is determined to a considerable extent by the electronic state of transmitting link B. Because of the substantial effect of the π-electron polarizability on the overall electronic conduction of the system, the presence of conjugated bonds in the bridge grouping increases its capacity for transmission of the electronic effect as compared with a polymethylene link of corresponding length.

The results of the present investigation make it possible to assert that a comparison of the numerical values of the polarographic $\rho_\pi$ constants, measured in the absence of side electrochemical effects, enables one to make an approximate estimate of the values of the effect of the conduction of the B grouping situated between the electrically active reaction center and substituent X. This aids one in predicting the reduction potentials and other reactivity parameters of as yet unsynthesized compounds of the furan series.

## EXPERIMENTAL

Distilled or freshly recrystallized compounds were used to prepare the starting solutions in water, ethanol, and DMF. The working solutions were prepared [14-16] by the addition of a Britton–Robinson buffer solution to the starting aqueous or aqueous-alcohol solutions or by the addition of LiCl to the starting solutions in DMF, during which the depolarizer concentration was brought up to $2 \cdot 10^{-4}$ M. The polarography was performed in a three-electrode cell [17] with forced detachment of the drops with the following characteristics: m = 0.98 mg/sec, t = 0.15 sec; with an external calomel electrode as the anode. The $E_{1/2}$ values were determined with an accuracy of ± 5 mV. The polarographic measurements were made with an LP-60 polarograph. The experimental $E_{1/2}$ values obtained were used to construct $E_{1/2}-\sigma$ graphs, from the slopes of the lines of which the $\rho_\pi$ constants for different experimental conditions were calculated from formula (1). Several of the starting $E_{1/2}$ values used to obtain the Hammett correlations were presented in [6, 7].

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